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One step fabrication of ZIF-8/polymer composite spheres by a phase inversion method for gas adsorption

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Abstract

This paper reports a phase inversion method for the preparation of macroporous polysulfone (PS) composite spheres through a single orifice spinneret. Surfactant F127 was pre-added in the polymer solution as a surface pore-forming agent, and different amount of zeolitic imidazolate framework-8 (ZIF-8) particles were incorporated to form the ZIF-8/PS composite spheres. ZIF-8 and polymer acted as the adsorbent and binder in the final composite spheres, respectively. The fabrication conditions, such as the types of the surfactant, the amount of the surfactant and ZIF-8 added in the polymer solution were investigated. Nitrogen and carbon dioxide sorption analysis indicated the ZIF-8/PS composite spheres had similar properties as the pure ZIF-8 particles, and the active sites of ZIF-8 in the polymer composites were well exposed. The composite spheres exhibited advantages of easy handling and recycling over ZIF-8 particles, and this phase inversion method can be extended to prepare other polymer composite spheres.

Keywords: Polysulfone; Zeolitic imidazolate framework; Composite sphere; Gas adsorption

1. Introduction

With the rapid increase of global population and the industrialization of more and more countries, the consumption of energy is explosively growing [1]. Carbon dioxide separation is a key step in carbon sequestration for preventing global warming [2]. Adsorption is one of the most important methods to separate compounds from the industrial gas mixtures, where columns packed with adsorbents are mainly utilized. The most common forms of adsorbents are the beads and the granules, consisting of small crystals (e.g. 1-10 μm in size) agglomerated into a desired shape and size using binder materials. The adsorbent materials are restricted to porous materials with a high surface/volume ratio, having pore sizes ranging from several Angstroms to a few tens of Angstroms. Thus, not only should the adsorbent materials be considered, but also how to make it easily apply in applications, in terms of handling and recycling, is a big problem.

Metal-organic frameworks (MOFs), a class of porous crystalline materials consisting of metal ions linked together by organic bridging ligands, have attracted considerable attention in recent years [3,4]. Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs, often show better thermal, hydrothermal and chemical stabilities [5-7]. All these properties make ZIFs be attractive in many applications, such as adsorption, separations, purifications and catalysis. ZIFs with sodalite topology including ZIF-7, ZIF-8, and ZIF-90 are of interests due to their mono-modal pore size distributions [8]. In particular, ZIF-8 is one of the most studied materials because of its potential functional applications, such as carbon dioxide adsorption due to its low density and high surface area [9-12].

In practical applications of ZIFs, it is not possible to directly use powder-form particles [13]. ZIFs could be prepared as thin-films or membranes through in-situ or seeding growth method for gas separation [14-16]. Another approach is to shape ZIFs (MOFs) into spheres or beads which have advantages over powder due to their easy handing and recyclability [13]. A series of metal organic frameworks have been deposited into millimeter-sized macroporous polyacrylamide (PAM), oxide or oxide-PAM. The resulting composites displayed enhanced mechanical stability and improved recyclability [13]. Shaping of ZIFs in millimeter-sized alumina beads was investigated by Aguado’s group for adsorption and catalytic applications [17]. Till now, there was no one-step method to prepare ZIF composite beads. However, there are various methods to prepare polymer beads. For example, monodisperse emulsion-templated polymer beads with an average diameter of 2.16 mm were prepared by oil-in-water-in-oil sedimentation polymerization [18,19]. Zhou et al. prepared cellulose/chitin beads by the coagulation method and used them for adsorption of heavy metals in aqueous solution [20]. Phase inversion method is one of the most important means to prepare asymmetric membranes, which was first developed by Loeb and Sourirajan [21]. Recently, we reported a new phase inversion method for the direct preparation of ultrafine hollow fiber membranes from a polymer solution using a single orifice spinneret [22]. This method inspired us to explore the possibility for the fabrication of porous millimeter-sized polymer spheres or beads in a one-step process.

In this work, we report a phase inversion method for the preparation of ZIF-8/polysulfone (ZIF-8/PS) composite spheres from a polymer solution containing ZIF-8 crystals using a single orifice spinneret. This is a one-step method to synthesize ZIF-8 composite spheres with polymer as the binder, and the size of the composite spheres is controllable. The addition of surfactants in the polymer solution can influence the formation of porous structure [23]. Different amount of ZIF-8 powder is mixed with polymer solution, and then the resulting solution is injected through a syringe tip to a water tank to form composite spheres via solvent/water exchange (Fig. 1). The organic solvent (e.g. N-methyl-2-pyrrolidone) and the surfactant are soluble in water, and the final spheres only contain polymer as the structure binder and ZIF-8 as the adsorbent.

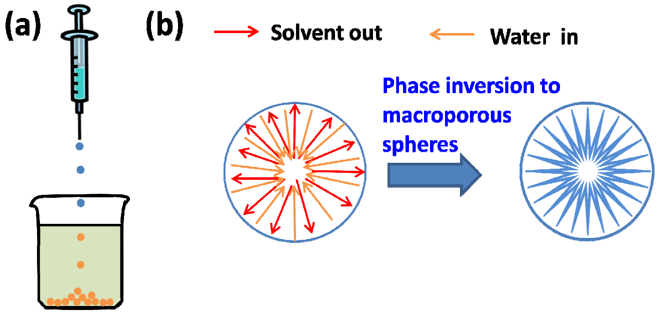

Fig. 1. Schematic diagrams of the phase inversion method for polymer sphere preparation through a single syringe tip (a), and the formation process of the porous structure via solvent/water exchange (b).

2. Experimental procedure

2.1 Chemicals

Polysulfone (average Mw ~35,000 by LS, average Mn ~16,000 by MO, pellets), N-methyl-2-pyrrolidone (99.5%, NMP), Pluronic F127, Pluronic P123, zinc nitrate hexahydrate, 2-methylimidazole (Hmim) were all purchased from Sigma-Aldrich. All of the chemicals were used as received without further purification.

2.2 Synthesis of ZIF-8 nanocrystals

Synthesis of ZIF-8 nanocrystals was performed following the reported recipe [9]. A solution of zinc nitrate (2.93 g) in 200 ml of methanol was mixed with a solution of Hmim (6.49 g) in 200 ml of methanol under stirring with a magnetic bar. The mixture turned to milky suspension after being stirred for 1h, and then the crystals were separated by centrifugation and washed with fresh methanol. Finally, the ZIF-8 crystals were dried at 50 ^{o}C overnight.

2.3 Preparation of polysulfone spheres and ZIF-8/polymer composite spheres by phase inversion method

A polysulfone solution was prepared by dissolving 0.75 g of polysulfone in 4.25 g of NMP. The mixture was stirred at room temperature overnight to make sure the polysulfone was completely dissolved. Then 0.1-1.0 g of surfactant P123 or F127 was added into the above polymer solution, and the whole solution was stirred several hours until it turned clear. The final solution was left for 2-3 h to allow complete release of bubbles. The polymer slurry was vertically pumped to a water tank through a fine stainless steel syringe tip with a size of 18 G (inner diameter of ~0.84 mm) at a flow rate of 0.2 ml/min. The air gap was of about 4 cm. Solid polymer spheres were formed immediately in water via solvent/water exchange (Fig. 1b). The resulting polymer spheres were kept in water overnight to leach out the residual NMP. Finally, the spheres were dried at 80 ^{o}C for 5 h.

ZIF-8/polymer composite spheres were prepared with the same procedure as above using F127 as the surfactant through a syringe tip with a size of 14 G (~1.6 mm). Three samples were prepared with different ZIF-8/PS weight ratio of 1:1, 2:1, and 4:1, and they were denoted as ZIF-8/PS 1:1, ZIF-8/PS 2:1 and ZIF-8/PS 4:1, respectively.

2.4 Characterization

Scanning electron microscopy (SEM) images were taken with a JEOL-7001F microscope operated at an accelerating voltage of 15 kV. Elemental analysis was performed using Energy-dispersive X-ray spectroscopy (EDX) on a JEOL JSM 7001microscope. X-ray diffraction (XRD) patterns of the samples were taken on a Philips PW 1140/90 diffractometer with Cu Kα radiation (25 mA and 40 kV) at a scan rate of 2^{o}/min with a step size of 0.02^{o}. The pore size distributions of the samples were measured by mercury porosimetry (Auto pore III mercury porosimeter, Particle and Surface Sciences Pty. Ltd. USA). The pore properties of the ZIF-8/PS spheres were measured by an ASAP 2020 adsorption porosimeter at a liquid nitrogen temperature of 77 K. Samples were degassed for 2 h at 100 ^{o}C under vacuum before analysis. The Brunauer-Emmet-Teller (BET) surface area was obtained. The carbon dioxide adsorptions of samples were taken with an ASAP 2010 adsorption analyzer at 273 K.

3. Results and discussion

3.1 Formation of polysulfone spheres with surfactant

Polysulfone spheres were prepared via a phase inversion method by injecting the polymer solution from a single orifice spinneret. The purpose of the addition of surfactant F127 and P123 in the polymer solution is to form a porous outer surface on the spheres. As both F127 and P123 are triblock copolymers (PEO-PPO-PEO) with hydrophilic and hydrophobic blocks, they could change the local chemical environments in the phase inversion process. F127 has a higher PEO weight percentage than P123, indicating F127 has more hydrophilic groups [24]. Fig. 2 shows SEM images of the surfaces of PS spheres prepared using different amount of surfactant (0.1-1.0 g) with the surfactant/PS weight ratios of 0.13, 0.33 and 1.33. For the PS spheres prepared with surfactant F127, Figs. 2a and b show the spheres have smooth surfaces and small pores on them. The surface pore size is about 0.2 µm for the PS spheres prepared with F127/PS weigh ratio of 0.33 (Fig. 2b), which is larger than that prepared with F127/PS weigh ratio of 0.11 (Fig. 2a). Fig. 2c shows the surface of the PS sphere is rough, and no apparent pores are observed on the surface. On the contrary, SEM images (Figs. 2d, e) show that the surfaces of the spheres prepared with P123/PS weight ratio of 0.11 and 0.33 are much different with that prepared with surfactant F127, where almost no pores present on the surface. For comparison, the surface of PS sphere prepared without addition of any surfactant was tested by SEM, and there are no pores on the surface (Fig. 2f) that is consistent with the literature [22,25]. The surface of PS spheres shown in Figs. 2e has a similar structure as that in Fig. 2f, indicating surfactant P123 could not change the surface properties of PS spheres.

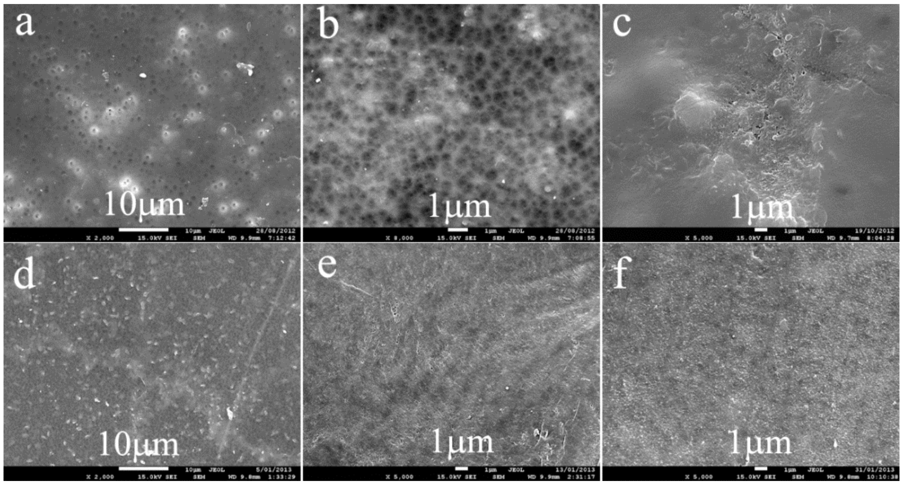

Fig. 2. SEM images of the surface structure of the PS spheres prepared using different amount of F127 (a-c) and P123 (d,e) and without any surfactant (f): the F127/PS weight ratio of 0.13 (a), 0.33 (b), (c) 1.33 (c); the P123/PS weight ratio of 0.13 (d), 0.33 (e).

Fig. 3 shows the detailed SEM images of PS spheres prepared with F127/PS weight ratio of 0.33. Fig. 3a shows the overall cross-section of the sphere, indicating there are a lot of channels in the sphere. Fig. 3b shows the inner channels of the sphere, presenting a finger-like pore structure. Fig. 3c shows an enlarged area of the channels of the sphere, indicating that the channels are consisted of macropores, and the average pore size is around 5 µm. These uniform macroporous structure would provide enough space for ZIF-8 particles loading and gas diffusion.

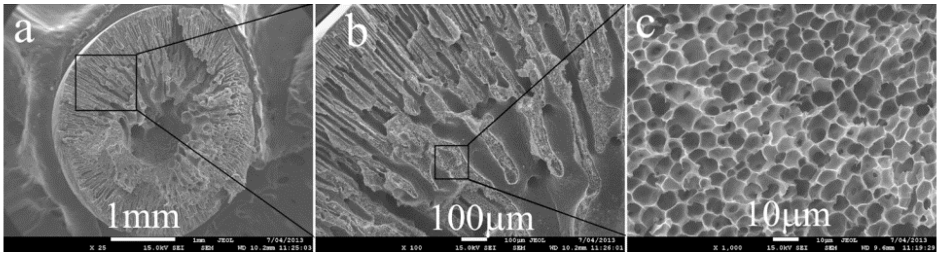

Fig. 3. SEM images of the cross-section view of the sphere prepared with the F127/PS weight ratio of 0.33.

The pore size distribution of the PS spheres prepared with F127/PS weight ratio of 0.33 shows two ranges of pores with sizes of around 1 µm and 5 µm (Fig. 4), which is consistent with the SEM results (Fig. 3c). The pore sizes are a little larger than the pure PS spheres prepared without surfactant (Fig. 4), indicating surfactant F127 could increase the pore size of the spheres, and the large porous structure would be favorable to accommodate ZIF-8 particles.

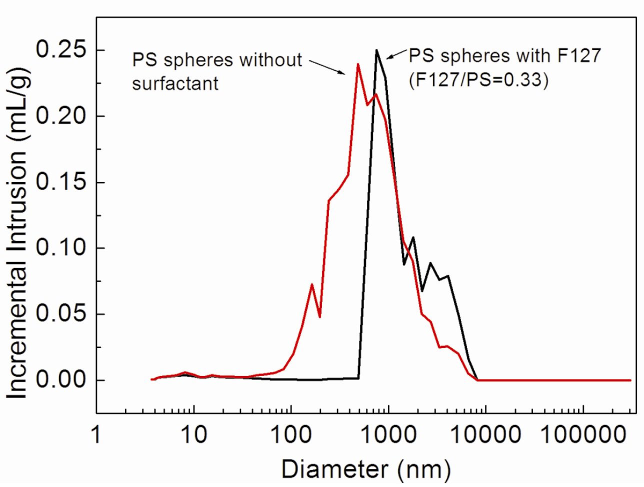

Fig. 4. Pore size distribution curves of the samples prepared with surfactant F127 and without surfactant.

The digital photos of pure PS spheres and PS sphere prepared with F127/PS weight ratio of 0.33 are shown in Figs. 5a, b. Both of them show a regular spherical shape with a narrow diameter distribution. The diameter of spheres is around 2.5 mm, which could be adjusted by changing the syringe tip sizes. The spheres are both in white color with a smooth surface. Furthermore, the addition of surfactant F127 makes the surface (Fig. 5a) much smoother, and a "handgrip" is disappeared compared to Fig. 5a. In the following study, F127 was used as the surfactant (F127/PS weight ratio of 0.33) to the synthesis of ZIF-8/PS composite spheres.

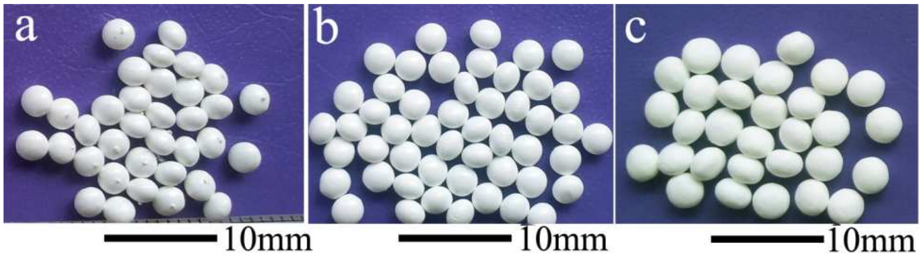

Fig. 5. Digital photographs of pure PS spheres (a), PS spheres prepared with surfactant F127 (b), and ZIF-8/PS 2: 1 spheres (c).

3.2 Incorporation of ZIF-8 nanocrystals in PS spheres

ZIF-8 powder was dispersed into the PS/NMP/F127 solution to form viscous slurry for the further sphere formation via the phase inversion method. Fig. 6 shows XRD pattern and SEM image of the ZIF-8 powder, indicating a high crystalline structure. The ZIF-8 particles have a narrow particle size distribution with an average size of about 80 nm. The weight ratio of ZIF-8/PS was varied from 1: 1 to 2: 1 and 4: 1. The final spheres were analyzed by XRD to examine the stability and presence of ZIF-8 in the system (Fig. 7). XRD patterns show that characteristic peaks of ZIF-8 appear [6], indicating that ZIF-8 is successfully loaded into PS spheres. In addition, with the increase of ZIF-8 amount, the intensity of ZIF-8 peaks becomes stronger. ZIF-8/PS 2:1 spheres have a regular spherical structure with a diameter of about 3 mm (Fig. 5c). The ZIF-8/PS 2:1 spheres were also analyzed by SEM to identify the morphology of the sphere as shown in Fig. 8. A porous structure is observed in Figs. 8a, b. The high magnification image in Fig. 8d shows ZIF-8 particles are evenly distributed on the pore structure of the sphere, where the diameter of the ZIF-8 particles is around 80 nm [9]. The inset in Fig. 8d indicates some ZIF-8 nanoparticles are located on the

PS surface, and others should be embedded in the polymer wall. The EDX point analysis result in Fig. 8c shows the Zn, N elements are existed, which confirms that these small particles are ZIF-8. Element S belongs to polysulfone.

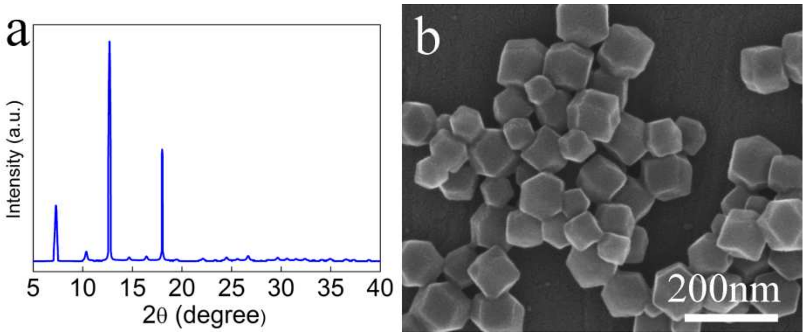

Fig. 6. XRD pattern (a) and SEM image (b) of ZIF-8 nanocrystals.

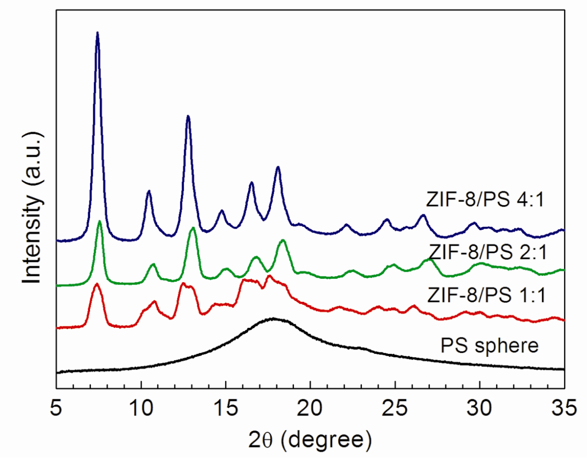

Fig. 7. XRD patterns of PS sphere and ZIF-8/PS composite sphere prepared with different weight ratio of ZIF-8/PS.

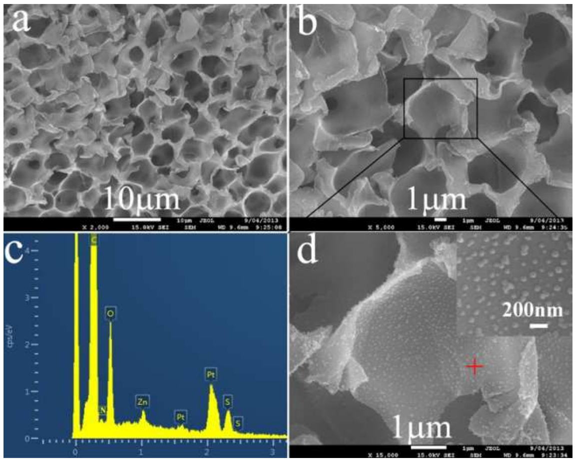

Fig. 8. SEM images of the cross-section view of a ZIF-8/PS 2: 1 sphere in different magnifications, and EDX pattern (c) of one point in (d), the inset in (d) shows some ZIF-8 nanoparticles on the PS surface.

3.3 Gas sorption of ZIF-8/PS composite spheres

The porosity of the ZIF-8/PS composite spheres was evaluated by nitrogen sorption measurements. The BET surface areas of PS spheres prepared without ZIF-8 and pure ZIF-8 particles are 4.5 and 1023 m^2/g, respectively (Fig. 9). The BET surface area of pure ZIF-8 particles is very similar to the literature [9] (962 m^2/g), but is lower than the corresponding value for microsized ZIF-8 reported by Park and co-workers [6]. This indicates that the as-synthesized ZIF-8 nanoparticles probably still contain some residual species in the cavities [9]. When ZIF-8 was added in the PS spheres, the BET surface area of the ZIF-8/PS spheres increased with the increase of ZIF-8 amount. ZIF-8/PS 4:1 spheres have a BET surface area of 761 m^2/g that is about 74% of the pure ZIF-8, indicating ZIF-8 particles are successfully incorporated in PS spheres and their active sites are well exposed. ZIF-8/PS 2:1 spheres have a BET surface area of 603 m^2/g that is 59% of the pure ZIF-8. ZIF-8/PS 1:1 spheres show a very low BET surface area of 128 m^2/g, which is only about 13% of the pure ZIF-8. The low surface area suggests ZIF-8 particles have excellent adhesion with the polymer matrix [26] and most of their active sites are hidden. ZIF-8/PS 1:1 spheres are not suitable for gas adsorption.

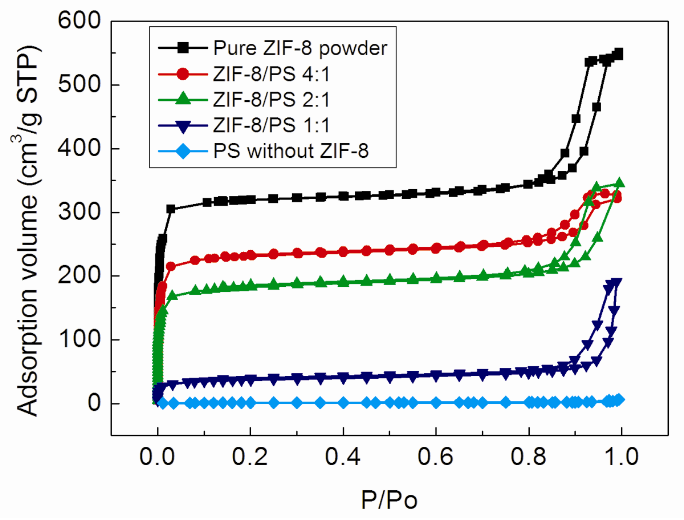

Fig. 9. Nitrogen adsorption-desorption isotherms of pure ZIF-8 powder, PS spheres and ZIF-8/PS composite spheres.

Fig. 10 shows carbon dioxide adsorption and desorption of pure ZIF-8 powder and ZIF-8/PS spheres at 273 K. The adsorption volume of pure ZIF-8 powder is about 33.5 cm^3/g at 116 kPa. ZIF-8/PS 4:1 and ZIF-8/PS 2:1 show CO_2 adsorption of 27.2 and 21.2 cm^3/g, which are about 81% and 63% of the pure ZIF-8, respectively. The CO_2 sorption further confirmed that ZIF-8 particles are well dispersed in PS spheres, and the active sites of ZIF-8 are well exposed. However, for ZIF-8/PS 1:1, the CO_2 sorption is only 11.6 cm^3/g that is about 35% of the pure ZIF-8. This result also indicates the active sites of ZIF-8 particles should be blocked by polysulfone.

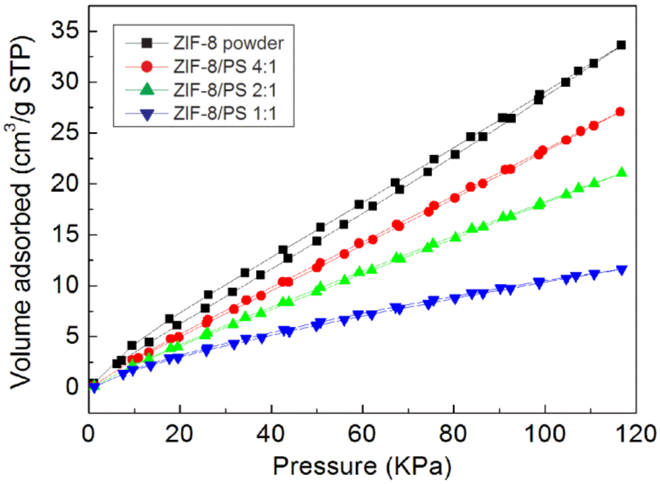

Fig. 10. Carbon dioxide sorption isotherms of pure ZIF-8 powder and ZIF-8/PS composite spheres.

4. Conclusion

We successfully fabricated ZIF-8/PS composite spheres via phase inversion method using a single orifice spinneret. Surfactant F127 was added in the system to improve the porosity of the spheres. The polysulfone structure and ZIF-8 acted as binder and adsorbent, respectively, and the porous structure of the sphere made the gas easily diffuse. ZIF-8/PS composite spheres were easy to handle and recycle, and the gas sorption ability of the ZIF-8/PS 4:1 and ZIF-8/PS 2:1 composite spheres were comparable to the pure ZIF-8. This method is a one step technique to prepare macroporous ZIF-8/PS composite spheres, and can be extended to prepare other polymer composite spheres.

Acknowledgments

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